

[0005]

[Means to Solve the Problems]

The present invention provides a method for producing a perovskite composite oxide powder represented by formula (1):



[wherein A represents at least one alkaline earth metal and B represents at least one tetravalent metal element], comprising adding at least one tetravalent metal compound and an alkali equivalent to or in excess of the tetravalent metal while stirring to at least one water slurry of a hydroxide of an alkaline earth metal, allowing the reaction to proceed, and ripening the obtained slurry containing the reactant at about 50 to 200°C, preferably about 100 to 200°C, for 0.1 to 10 hours, preferably about 0.1 to 3 hours.

[0006]

The present invention is a method of performing a coprecipitation reaction at an ordinary temperature using an inexpensive starting material and thereafter performing a ripening treatment, preferably a hydrothermal treatment, to obtain a perovskite crystal having extremely high completeness. The crystal obtained by the method of the present invention is fine particles having an average primary particle size of approximately from 0.01 to 1  $\mu\text{m}$  and moreover, this crystal scarcely undertakes aggregation. Therefore, the average secondary particle size is as small as approximately from 0.01 to 1  $\mu\text{m}$  and the crystal can have

an extremely high dispersibility. Furthermore, the primary particle size distribution and the secondary particle size distribution are sharp and also, the primary particle and the secondary particle both have an almost spherical outer shape, so that the crystal powder can exhibit good fluidity and high filling property. Accordingly, when the powder obtained by the method of the present invention is used, a high-performance ceramic can be easily provided. The hydroxide of an alkaline earth metal for use in the present invention means a hydroxide of Mg, Ca, Sr or Ba. Examples of the tetravalent metal element for use in the present invention include Ti, Zr and Sn. Examples of the tetravalent metal compound include halides of these metals, such as chloride and bromide, and water-soluble monovalent salts such as nitrate. Examples of the alkali component for use in the present invention include alkali metal hydroxides such as sodium hydroxide, potassium hydroxide and lithium hydroxide, and organic amines such as ammonium hydroxide, dimethylamine and N-N'-dimethylbenzylamine.

[0007]

The alkali component may be added at any stage, namely, before the addition of an aqueous tetravalent metal compound solution to a water slurry of an alkaline earth metal hydroxide, simultaneously with the addition of the aqueous solution, or after the addition. The amount of the alkali component added may be sufficient if it is almost equivalent to or greater than the tetravalent metal compound. In order not to cause carbonation of the alkaline

earth metal hydroxide during the coprecipitation reaction and the subsequent ripening reaction, carbonate ion and carbon dioxide in water used or in the atmosphere are preferably removed as much as possible. The stirring at the coprecipitation reaction is a necessary operation and the ripening treatment reaction is also preferably performed under thorough stirring. After the ripening treatment, the slurry is filtered, washed and dried in a usual manner, as a result, perovskite crystal fine particles having high dispersibility can be obtained. The dried product may be further calcined at about 800°C, then washed and dried. In the washing, pure water from which carbonate ion and the like are removed is preferably used.

[0008]

In the present invention, an aqueous solution containing a water-soluble salt of a rare earth element known for the semiconducting formation, such as Y, Sc and La, or an element such as Bi, Nb and Sb, may also be added at the coprecipitation reaction and participated in the coprecipitation reaction. At this time, the alkali component is preferably added in an amount increased by the portion equivalent to the element added. According to the method of the present invention, the obtained crystal of perovskite composite oxide  $ABO_3$  can be substantially free of aggregation and advantageous in that the primary particle size and the secondary particle size are almost equal, the average secondary particle size is approximately from 0.01 to 1.0  $\mu\text{m}$ , preferably about 0.01 to 0.5  $\mu\text{m}$ , and

the BET specific surface area is about 1 to 20 m<sup>2</sup>/g. The method for producing a perovskite composite oxide of the present invention can solve the problem of conventional production methods, that is, generation of heterogeneous precipitation due to the great difference in the pH necessary for the formation of a hydroxide at the precipitation reaction, between an alkaline earth metal and a tetravalent metal element compound. More specifically, in the production method of the present invention, an alkaline earth metal element having high solubility and not forming a hydroxide unless the pH is high is prepared as a hydroxide from the beginning and to this hydroxide, an aqueous tetravalent metal solution and an alkali component are added to enable the proceeding of a nearly ideal coprecipitation reaction, so that the problem encountered in conventional production methods can be solved. As a result, a coprecipitate having a composition close to a perovskite composite oxide can be obtained and a production method capable of easily producing, through the subsequent hydrothermal reaction in the liquid phase, a perovskite composite oxide crystal at a low temperature as compared with conventional production methods while ensuring high completeness can be provided.

[0010]

The present invention is described in greater detail below by referring to Examples. In the following Examples, unless otherwise indicated, the "parts" and the "%" mean "parts by weight" and "% by weight", respectively.

#### Example 1

To 500 ml of deionized water (about 25°C), 0.1 mol of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  was added while stirring and thereby dispersed and dissolved. Thereto, 0.1 mol of  $\text{TiCl}_4$  solution (about 25°C) and subsequently, 0.4 mol of an aqueous solution (about 25°C) containing 4 mol/liter of sodium hydroxide were added and the resulting solution was held for 0.25 hours while stirring. The slurry obtained by this reaction was charged into an autoclave as it was and then subjected to a hydrothermal treatment at 170°C for 2 hours, filtration under reduced pressure, washing with deionized water and drying. The obtained barium titanate powder was analyzed by X-ray diffraction and found to be a cubic crystal. In the particle size distribution by a laser diffraction scattering method, the average particle size was 0.106  $\mu\text{m}$  and the standard deviation was 0.016  $\mu\text{m}$ , revealing that the powder was a very fine particle and the distribution width was narrow. The BET specific surface area was 6  $\text{m}^2/\text{g}$ . The powder was also observed by a scanning electron microscope, as a result, almost all particles were spherical and the particles having an average diameter of about 0.1  $\mu\text{m}$  were dispersed without causing aggregation. Fig. 1 is an

electron microphotograph ( $\times 10,000$ ) showing the crystal structure of the obtained powder and Fig. 2 shows the particle size distribution.

[0011]

#### Example 2

To 500 ml of deionized water (about 25°C), 0.06 mol of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and 0.04 mol of  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  were added while stirring and thereby dispersed and dissolved. Thereto, 0.095 mol of  $\text{TiCl}_4$  solution (about 25°C) and subsequently, 0.4 mol of an aqueous solution (about 25°C) containing 4 mol/liter of sodium hydroxide were added and the resulting solution was kept for 0.25 hours while stirring. The slurry obtained by this reaction was charged into an autoclave as it was and subjected to a hydrothermal treatment at 150°C for 2 hours, filtration under reduced pressure, water washing and drying. The obtained powder having a composition of  $(\text{Ba}_{0.60}\text{Sr}_{0.40})\text{TiO}_3$  was analyzed by the X-ray diffraction and found to be a cubic solid solution having the same crystal structure as  $\text{BaTiO}_3$ . In the particle size distribution, the average particle size was 0.122  $\mu\text{m}$  and the standard deviation was 0.024  $\mu\text{m}$ . The BET specific surface area was 8.5  $\text{m}^2/\text{g}$ . The powder was also observed by a scanning electron microscope, as a result, almost all particles were spherical and the particles having a diameter of about 0.1  $\mu\text{m}$  were dispersed without causing aggregation.

[0012]

Example 3

To 500 ml of deionized water (about 20°C), 0.1 mol of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  was added while stirring and thereby dispersed and dissolved. Thereto, 0.4 mol of an aqueous solution (about 20°C) containing 4 mol/liter of potassium hydroxide was added and subsequently, 0.09 mol of  $\text{TiCl}_4$  solution (about 20°C) and 100 ml of an aqueous solution (about 20°C) having dissolved therein 0.01 mol of  $\text{SrCl}_4$  were simultaneously added. The resulting solution was heated at 70°C and kept for about 2 hours while stirring. The obtained slurry was filtered under reduced pressure, washed with deionized water and then dried. The obtained powder having a composition of  $\text{Ba}(\text{Ti}_{0.90}\text{Sr}_{0.10})\text{O}_3$  was analyzed by the X-ray diffraction and found to be a cubic solid solution having the same crystal structure as  $\text{BaTiO}_3$ . In the particle size distribution, the average particle size was 0.196  $\mu\text{m}$  and the standard deviation was 0.058  $\mu\text{m}$ . The BET specific surface area was 12.1  $\text{m}^2/\text{g}$ . The powder was also observed by a scanning electron microscope, as a result, almost all particles were spherical, the diameter thereof was about 0.2  $\mu\text{m}$  and the particles were dispersed without causing aggregation.

[0013]

Comparative Example 1

To 500 ml of deionized water (about 20°C), 0.12 mol of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  was added under stirring and thereby dispersed and dissolved. Thereto, 0.1 mol of  $\text{TiO}_2$  was added,

dispersed and dissolved, and the resulting solution was held for about 0.25 hours while stirring. The obtained slurry was charged into an autoclave and then subjected to a hydrothermal treatment at 170°C for 2 hours, filtration under reduced pressure, washing with deionized water and drying. The powder obtained was analyzed by the X-ray diffraction and found to be a mixture of cubic barium titanate and titanium oxide.